

# Preliminary test on modified clays for seawater resistant drilling fluids

## Essais préliminaires sur les argiles modifiées pour fluides de forage résistant à l'eau de mer

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**ABSTRACT** The quality of a drilling fluid declines in salt water conditions. An engineered clay (HYPER clay) was developed for geosynthetic clay liners with enhanced resistance to aggressive conditions. This study investigates the potential of this superior clay for drilling fluids applied in salt water conditions. A sodium bentonite was treated with a carboxymethyl cellulose (CMC) polymer following the HYPER clay process method. Preliminary tests were performed to investigate suitability of HYPER clay for seawater resistant drilling fluids. Fluid performance was characterized by its thixotropic behavior, rheological properties (gel strength, yield point and viscosity), swell and bleeding behavior. Drilling fluid performance was analyzed at various polymer dosages and electrolyte concentrations. Polymer treatment improved the gel strength and swelling ability of the fluid, especially in electrolyte solutions. Moreover, filter press tests (API 13B-1, 76% seawater) showed that filtrate loss decreased due to polymer treatment.

**RÉSUMÉ** La qualité d'un fluide de forage diminue dans des conditions d'eau salée. HYPER clay, une argile modifiée possédant une meilleure résistance aux conditions agressives, a été développée pour les géosynthétiques bentonitiques. Cette étude examine le potentiel de cette argile pour les fluides de forage appliqués dans des conditions d'eau salée. Une bentonite de sodium a été traitée avec de la carboxyméthylcellulose (CMC) selon la méthode de traitement de la HYPER clay. Des essais préliminaires ont été réalisés pour étudier la pertinence de la HYPER clay pour des fluides de forage résistant à l'eau de mer. La performance du fluide a été caractérisée par son comportement thixotropique, ses propriétés rhéologiques (résistance du gel, seuil d'écoulement et viscosité), son gonflement et sédimentation. La performance du fluide a été analysée à divers dosage de polymère et concentrations d'électrolyte. Le traitement de l'argile avec polymère a amélioré la résistance du gel et la capacité de gonflement du fluide, en particulier dans les solutions électrolytiques. En outre, les essais en filtre-pressé (API 13B-1, 76% d'eau de mer) ont montré que la perte de filtrat diminue en cas de traitement avec polymère.

### 1 INTRODUCTION

The essential function of a drilling fluid is to stabilize the wellbore area during drilling and to transport the cuttings to the surface (Hughes et al, 1993; Kelessidis et al, 2007). The wellbore is stabilized by cake formation on the walls. The cake is formed by filtration of the drilling fluid which leaves the particles in the fluid on the wellbore surface. The dominant mechanism of filtration control is cake formation on the wellbore surface and not the subsequent growth of the filter cake (Rugang at al., 2014). Spurt loss refers to the filtrate lost in the formation during this primary stage of cake formation (Rugang at al., 2014). Good

filtration performance of the drilling fluid is required to stabilize the wellbore area. Filtration performance is expressed in a thin and impermeable filter cake.

The ideal drilling fluid has a low viscosity of optimum 20 cP to prevent high pressure differences along the length of the wellbore. For the transport of the cuttings to the surface, the fluid needs to have sufficiently high yield strength. The gel strength (the yield strength after standstill for some minutes) should be minimized though, to prevent high pump pressures when restarting.

Target properties for standard water based drilling fluids are set by the former OCMA standard (API, 2010). The filter cake should be slick and thin about

1 to 2 mm, and filtration losses of lower than 15 ml/30 minutes with an optimum at 13 ml/30 minutes should be obtained (performing Filter Press Test as described by API 13B standard, 2009). An absolute minimum yield strength of 15 lb/100 ft<sup>2</sup> is recommended (API, 2010). The gel should be no more than 6 to 10 lb/100 ft<sup>2</sup> after 10 seconds and 10 to 30 lb/100 ft<sup>2</sup> after 10 minutes is recommended (API, 2010).

### 1.1 Drilling fluids

Drilling fluids consist of suspended clay particles, the continuous phase (water) and optional treating agents for pH adjustment (soda ash), rheology and filtration control (polymers). The composition of drilling fluid and the hydration reactions of the clay, have a great effect on its rheological properties and filtration performance.

Sodium montmorillonite clays, referred to as sodium bentonites, are perfect to use in drilling fluids, given their high tendency to swell. The net surface charge of a clay particle is negative. This negative surface charge is balanced by exchangeable cations, typically Na<sup>+</sup> or Ca<sup>2+</sup>, in the interlayers, and a diffuse double layer at the outer surface of the particle. Swell indicates the attraction of ions and water molecules to the particle surface to counter balance this interlayer and outer layer negative surface charge. These adsorbed water molecules are essentially immobile and contribute to the low permeability and thixotropic behavior of bentonites (Barshad, 1960).

Thixotropy is time dependent flow behavior (Barnes, 1997). Thixotropic behavior is related to the build-up and breakdown of three dimensional network (also referred as the house-of-cards structure) (Huisman, 2010; Luckham et al., 1999). The resulting gel strength holds the cuttings into suspension, particularly when operations are interrupted (Yaln, 2002).

### 1.2 Inhibitory effect of electrolytes

For water based drilling mud the continuous phase is most often fresh ground or surface water. A local deficiency of fresh water, could result in the use of saline or brackish water as process water. Such water will contaminate the continuous phase with ions like sodium and calcium chloride, referred to as electrolytes. Water is considered to be fresh if it contains a

chloride concentration less than 150 mg/l. In turn water is considered to be brackish if it contains a chloride concentration of 150 mg/l up to 1000 mg/l (De Vries, 2007).

Already a chloride concentration of 165 mg/L, has an inhibitory effect on the clay hydration and dispersion is observed (Rugang et al., 2014). The addition of electrolytes to the system will compress the diffuse double layer. In other words, the energy barrier between dispersed clay particles is compressed and the agglomeration of clay particles is accelerated. As a result, particles associate in the form of a loose, open network (Rugang et al., 2014; Caenn et al, 2011). This structure persists to a limited extent in filter cakes, causing a considerable increase in permeability (Stamatakis and Tien, 1991). Moreover, agglomeration will cause the clay suspension to be unstable and phase separation will occur. The rheology of the drilling fluid changes dramatically and the fluid loses its functionality (Yaln et al., 2002). Therefore, it is necessary to develop optimized bentonites for water based drilling fluids with the following characteristics: compatible with electrolytes and able to support drilling conditions. The purpose of this research is to investigate if clays treated with HYPER clay technology could fulfill these requirements.

### 1.3 HYPER clay elevated resistance to electrolytes

HYPER clay is an carboxymethyl cellulose treated bentonite as introduced by Di Emidio (2010) for use in geosynthetic clay liners. With the HYPER clay procedure the polymer is adsorbed to the clay sheets due to a dehydration step. The polymer is intercalated between the clay sheets. Thereby the diffuse double layer thickness (i.e swell capacity) can be maintained even in electrolyte systems. The HYPER clay particles maintain their long range repulsive energies in electrolyte systems.

Given the improved hydraulic performance of HYPER clay in concentrated systems as GCL pastes (> 80% w/w), (Di Emidio 2010), HYPER clay could have an elevated resistance to electrolytes and maintain optimal filtration performance even in dilute systems as drilling fluids are (d.s. 3 – 6 % w/w). For this reason the focus of this work was to evaluate if HYPER clay could be suitable as base clay in electrolyte resistant drilling fluids.

## 2 MATERIALS

### 2.1 Syntheses of HYPER clay

The base clay is a high quality sodium montmorillonite, which is also known as Wyoming bentonite (Product name Natural Gel). Physical and chemical composition of Natural Gel have been listed by De Jaegher (2013).

The anionic polymer carboxymethyl cellulose (CMC) is used to treat the clay. CMC is a highly charged anionic polyelectrolyte with carboxylic acid groups located on its cellulosic backbone. The counter ion for the anionic groups is sodium. The indicated Brookfield viscosity is 400 up to 100 Pas.

To produce HYPER clay, Natural Gel was treated with Sodium carboxymethyl cellulose (Na-CMC) at various dosages (from 14%, 18% and 25% dry weight clay). For a detailed description of HYPER clay production method we refer to Di Emidio (2010). Di Emidio (2010) used polymer dosages of 2% up to 10% dry weight clay, and a water to clay ratio of 10 (W/C). To compensate for the higher polymer concentration used in present study, more water was required to dissolve the polymer. Therefore, W/C in this study was 20.

To access the quality of the HYPER clays produced, the swelling potential was determined in accordance with ASTM D5890. The swell index test gives an indication of the maximum swell capacity of a clay. The swelling capacity of Natural Gel was elevated due to polymer treatment and increased with polymer dosage. The swell indexes observed were 26, 40.5, 46.8 and 53.3 ml per 2 gram, at a polymer dosage of 0%, 14%, 18% and 25% respectively.

### 2.2 Drilling fluid formulation

The drilling fluids formulated are presented in Table 1. Brine based fluids were prepared containing 3.6% to 4.5% solids by weight. As source of electrolytes for preparation of the salt water based mud, sea water from Oostende, Belgium was collected and filtered before use. The final sea water percentage was varied from 40% up to 76% by volume process water (Table 2). Composition analyses of Oostende sea water can be found in Di Emidio et al. (2011).

**Table 1.** Drilling fluids formulated

Sample	Composition	Clay concentration	Seawater	EC
		wt. %		
#	code	process water	% v/v	mS/cm
untreated				
1	NG_3,6%_24	3.6%	49%	24
1	14%HC_3,6%_20	3.6%	40%	20
2	14%HC_3,6%_30	3.6%	61%	30
3	18%HC_3,6%_20	3.6%	40%	20
4	18%HC_3,6%_30	3.6%	61%	30
5	25%HC_3,6%_20	3.6%	40%	20
6	25%HC_3,6%_30	3.6%	61%	30
untreated				
2	NG_4,5%_37	4.5%	76%	37
7	14%HC_4,5%_37	4.5%	76%	37
8	18%HC_4,5%_36	4.5%	73%	36

The salt water based muds were initially prepared from a paste based on HYPER clay solids (15% – 16% wt. solids) and deionized water. Referred to as the prehydration step. The paste was hydrated for 30 minutes. Subsequently a mixture of sea and deionized water was added to obtain the aimed solid concentration of the drilling fluid. Following this process method, a stable suspension was obtained at elevated electrolyte concentration up to 37 mS/cm. The drilling fluids were mixed for 5 minutes using a high shear mixer, MP550, and aged for 24 hours at 20 °C ( $\pm 2$  °C). Chemical properties of the process solutions used are presented in Table 2.

**Table 2.** Chemical properties of process waters

Solution	EC	pH
	mS/cm	-
Seawater (100%)	44.8	7.42
Diluted seawater (76%)	37.0	7.43
Diluted seawater (61%)	30.2	7.48
Diluted seawater (40%)	20.4	7.53

## 3 METHODS

Drilling fluid performance was characterized by suspension stability, its thixotropic and rheological properties (gel strength, yield point and viscosity), and filtration performance; tested in accordance with API 13-b Recommended Practice for Water Based Drilling Fluids (API, 2009). Each sample was stirred

for 5 minutes before rheological and filtration properties were measured.

An indication of suspension stability was obtained by measuring the volume of 'free water' after 24 hours of incubation at constant temperature  $20\text{ }^{\circ}\text{C} \pm 1$ . The fluid was poured in a glass cylinder 1.5 hour after preparation, covered and left to rest. After 24 hours the final temperature and suspended solids height were registered. The volume of free water was calculated as volume free water over total volume.

Filtration performance was determined by following the API Fluid Loss Test, the standard static filtration test used in the industry (API 13B, 2009). With the addition that in our tests the weight of filtrate was recorded continuously (interval of 1/6 seconds).

Rheological tests conducted in this study are based on the procedures recommended by the American Petroleum Institute (API, 2009). Rheology properties were determined using a Fann (model 35 SA) viscometer. A so called consistency curve displays the relationship between shear rate and shear stress. The apparent viscosity (AV), plastic viscosity (PV), yield point (YP) and Gel strength after 10 seconds and 10 minutes were derived from this consistency curve in accordance with reference API 13B-1(2009).

## 4 RESULTS AND DISCUSSION

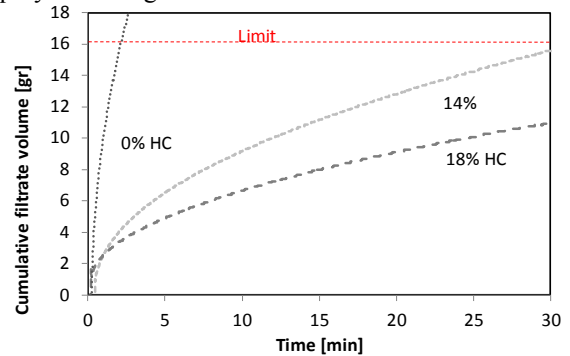
### 4.1 Stability of suspension

Polymer treatment following the HYPER clay procedure, including the prehydration step resulted in the creation of stable clay suspensions. No phase separation was observed 24 h and even 72 h after addition of the electrolyte contamination (20 mS/cm up to 37 mS/cm), as opposed to the untreated clay (free water volume was 17.7 and 22.3 ml / 100 ml for the drilling fluid untreated 1 and 2, see table 1, respectively). Therefore it could be concluded that the polymer adsorbed on the surface of the clay particles prevented aggregation at electrolyte contamination.

### 4.2 Filtration performance

Filter cake build-up and filtration performance of treated and untreated bentonites are compared based on the results shown in Table 3. HYPER clay results into reduced spurt and filtrate loss in an electrolyte contaminated system. At a higher clay concentration

(4.5%) the observed filtrate loss is still within acceptable limits using both 14% and 18% of polymer, despite the elevated chemical stress, i.e. electrical contamination of  $\sim 37\text{ mS/cm}$ . Moreover an increased resistance to electrolytes is observed with increasing polymer dosage.



**Figure 1.** The influence of polymer dosage on filtration performance of brine based drilling fluids, containing 4.5% solids by weight process water. Filtration performance is evaluated at 37 mS/cm.

**Table 3.** Filtration performance brine based drilling fluids

Sample	Composition	Vol_30	h
#	code	gr/ 30 min	mm
untreated 1	NG_3.6%_24	44.6	2.2
1	14%HC_3.6%_20	13.5	1.2
2	14%HC_3.6%_30	11.6	1.2
3	18%HC_3.6%_20	10.7	1.4
4	18%HC_3.6%_30	9.4	1.2
5	25%HC_3.6%_20	9.5	0.8
6	25%HC_3.6%_30	8.8	0.7
untreated 2	NG_4.5%_37	62.6	2.3
7	14%HC_4.5%_37	15.7	2.4
8	18%HC_4.5%_36	11.0	2.1

Legend: Vol\_30: Cumulative loss of filtrate over 30 minutes; h: Filter cake thickness.

Improved filtration performance is expressed in a reduced filter cake thickness and filtrate loss (see Table 3). These test results point out the suitability of HYPER clay for filtration control in brine based drilling fluids and/or in case of electrolyte contamination of the ground water (brackish: De Vries, 2007).

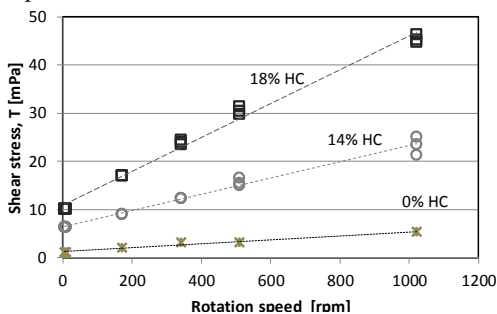
The observed increase in filter cake thickness with higher clay dosage independently of electrolyte concentration is in accordance with Rugang et al, (2014) and Calçada et al., (2011). At higher clay contents,

there is an increased probability that particles collide and that aggregates are formed.

The filter cake filtration performance of the untreated bentonite is not acceptable to function as a drilling fluid at 24 and 37 mS/cm, because the permeability of the cake is too high. The filtration rates do not cease over time. It is postulated that in the absence of the adsorbed polymer, electrolyte contamination causes coagulation of clay particles to such an extent that an open pore network is formed (Rugang et al., 2014).

The observed improved performance in high electrolyte systems is explained by the extended basal spacing (Di Emidio, 2010) upon polymer intercalation. This effect cultivates a preserved swelling capacity of the HYPER clays in electrolytes. The observations of Rugang et al. (2014) support these postulations. Based on SEM analyses of filter cakes, Rugang et al. (2014) relates an increase in filter cake permeability in the presence of electrolytes to increase of pore size and decrease in pore wall thickness.

Careful design of 'HYPER clay drilling fluid' is necessary to obtain the right rheological properties. A consequence of the HYPER clay procedure is a decrease in yield strength and an progressive gel strength (Figure 3). Sample no. 8 shows that it is possible to fulfill the requirements. Further research focuses on a further improvement of the rheological properties.

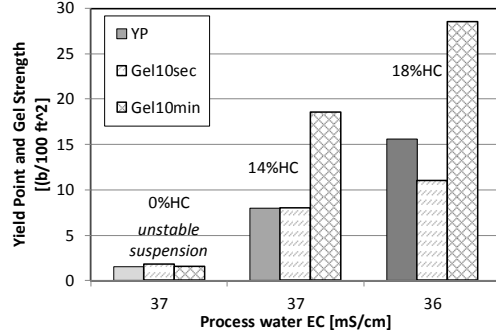


**Figure 2:** The influence of polymer dosage on the consistency curve of brine based drilling fluids, containing 4.5% solids by weight process water. Filtration performance is evaluated at 37 mS/cm.

#### 4.2.1 Consistency curve

Although the Herchel-Buckley equation is the common model to describe the consistency curve of bentonite based drilling fluids (Luckham and Rossi,

1999; Huisman, 2010), the results seem to be more consistent with the Bingham model (see figure 2) (Luckman and Rossi, 1991; Huisman, 2010; Bingham, 1922).



**Figure 3:** The influence of polymer dosage on Yield point and Gel strength of brine based drilling fluids, containing 4.5% solids by weight process water.

#### 4.2.2 Yield and Gel strength of the mud

**Error! Reference source not found.** illustrates the thixotropic properties of the drilling fluid no. 7 and 8. Yield point represents thixotropic behavior in dynamic state (association energies of particles after intensive mixing) and Gel Strength in static state (association energies of particles after a certain period of rest). An improved Yield Point was obtained by increasing the polymer dosage from 14% up to 18%, at electrolyte contamination of 37 mS/cm and solid concentration of 4.5% by weight process water. At a polymer dosage of 18% the lower limit of 15 lb/100 ft<sup>2</sup> was reached. In terms of Gel strength HYPER clay fulfills the requirements both at 14% and 18% polymer dosage.

As it was the case for filter cake thickness, higher clay contents increase the probability that particles collide and a three-dimensional network is formed (Rugang, 2014; Kretser and Boger, 2001). Therefore, the gel strength and yield at a clay concentration of 4.5% are higher than at 3.6%, even at a higher electrolyte concentration (18% polymer dosage: YP of 6.4 versus 15.6 lb/100 ft<sup>2</sup>; Gel strength at 10 min. of 12.7 versus 28.5 lb/100 ft<sup>2</sup>).

The yield strengths of the stable HYPER clay suspensions are equal to or below the set lower limit of 15 lb/100 ft<sup>2</sup>. The relatively low yield and gel strengths indicate that the total energy of interaction is dominated by long range repulsive forces. This



force is so high that particles only rarely link in an edge-edge or edge-face association. The formation of a three dimensional network (also referred as the house-of-cards structure) is therefore restricted.

Since the HYPER clay suspensions are stable (i.e. are not at the point of aggregation), it is postulated that the adsorbed polymer works as a thinning agent. In drilling practice phosphate salts are for instance used to increase fluid resistance to electrolytes and prevent the accompanying increase in yield up to the point of aggregation. The phosphate oxide groups sorp onto the exposed positive charged edges of the clay. Dissociation of the associated counter sodium ions than produces a negative edge surface. Preventing the build-up of gel structures by edge to face association (Olphen, 1997; Luckham and Rossi, 1999).

## 5 CONCLUSION

Polymer treatment according to the HYPER clay process method improved the filtration performance of a Wyoming bentonite in brine based drilling muds. At 14% polymer dosage the filtrate performance still fulfills the target as set by OCMA, at an electrolyte contamination of 37 mS/cm. Moreover, in terms of filtrate performance an increased resistance to electrolytes is observed with increasing polymer dosage up to 25% by clay weight. Therefore it could be concluded that HYPER clay has the potential to function as a base clay in brine based drilling fluids.

Ongoing research aims at two aspects specifically, regarding HYPER clay performance in a drilling fluid. At this stage a first hydration with low electrolyte water is still required to obtain a stable suspension. Furthermore, the in principle positive low viscosity of the HYPER clay based drilling fluids is accompanied by a relatively low yield and gel strength.

Research aims in particular on the various characteristics of CMC polymers, among which the degree of substitution, and its relation to HYPER clay performance. Using a polyanionic cellulose polymer to produce HYPER clay and a xanthan gum additive in the drilling fluid shows to be an effective method to obtain a stable suspension without prehydration and to obtain good carrying capacities. The results of current research will be published in March 2015 (den Hamer et al. 2015).

## ACKNOWLEDGEMENT

We gratefully acknowledge the financial support provided by the Industrial Research fund (IOF).

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